

DEPARTMENT OF TOXIC
SUBSTANCES CONTROL



ENVIRONMENTAL CHEMISTRY LABORATORY

**Mobile Laboratory Support to Site Mitigation:
Simplified Method for Measuring Toxaphene
Contamination by Gas Chromatography/Mass
Spectrometry with Selective Ion Monitoring**

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Mobile Laboratory Support to Site Mitigation: Simplified Method for Measuring Toxaphene Contamination by Gas Chromatography/Mass Spectrometry with Selective Ion Monitoring

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2/11/09

Date

EXECUTIVE SUMMARY

Although the primary responsibility of the DTSC Mobile Laboratory (ML) is to rapidly respond to any emergency in California, the ML also supports Site Mitigation projects on request. During January 22–25, 2007, the ML team was deployed to Dos Palos, CA to help in the investigation of a site (Central Valley Fertilizer) contaminated with toxaphene. A simplified screening method was developed to identify and measure toxaphene with a Limit of Quantitation (LOQ) of 0.5 ppm. Using this method, the ML team successfully completed the analysis of 36 soil samples in less than 3 days. Toxaphene was measured in 6 of those samples above the action limit (1.8 ppm) set for this site. These on-site measurements provided project managers with timely information. An extraction step will be added to this method in the near future and a comparison against standard methods will be undertaken.

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ABBREVIATIONS AND ACRONYMS

AMDIS = Automatic Mass Spectrum Deconvolution Identification Software

GC/ECD = Gas Chromatograph/electron capture detector

GC/MS = Gas Chromatograph/Mass Spectrometer

GC/MSD = Gas Chromatograph/Mass Selective Detector

NIMS = Negative Ion Mass Spectrometry

SIM = Selective Ion Monitoring

SOP = Standard Operating Procedure

TIC = Total Ion Chromatogram

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INTRODUCTION

The Department of Toxic Substances Control's (DTSC) Mobile Laboratory (ML) was funded by the Homeland Security Grant Program (HSGP). The primary duty of the ML team is emergency response. Because of its mobile deployment capabilities, the ML team is designated to quickly identify unknown chemical releases from natural disasters, industrial spills, explosions or terrorist attacks.

Site Mitigation Projects are a major part of DTSC's responsibilities. Ongoing projects are essential for the protection of public health and the environment within the state. One of the difficulties for most project managers is obtaining timely assessment information about the contaminated site and/or to locate on-site hot spots. The ML team can be instrumental in Site Mitigation projects (1). A core capability of the ML is to characterize site contamination with qualitative and quantitative chemical data in order to quickly supply project managers with critical information for on-site decision making and risk assessment. In response to a request from the Site Mitigation Branch Project Manager, the ML team was deployed to Dos Palos, County of Merced, California, on January 22-25, 2007.

METHODS

Site Description

The abandoned property belongs to the Central Valley Fertilizer Company and consists of a cement bed for washing pesticide spraying equipment and vehicles, a waste water collection basin and a half acre evaporation pond. The sample plan and abandoned site are presented in Figure 1. The scope of the assignment was to characterize the site for toxaphene contamination with the objective of procuring risk assessment information for future cleanup or litigation.

Approach

A simplified method to analyze soil samples for toxaphene was developed for this Site Mitigation project. The method utilized the on-board GC/MS with a SIM mode to quickly screen soil samples for toxaphene. The project manager required a limit-of-quantitation (LOQ) level of 1.8 ppm; therefore, the limit-of-detection (LOD) level was set at 3 times below that, i.e., at 0.5 ppm.

Materials and Reagents

1. Solvents – Pesticide grade (Thermo Fisher Scientific, Pittsburgh, PA).
2. Standard – Toxaphene, National Institute of Standards & Technology, Gaithersburg, MD 20899.
3. Internal Standard: 2-florobiphenyl (Supelco, 595 North Harrison Road, Bellefonte, PA).
4. Surrogate: decachlorobiphenyl (Supelco, 595 North Harrison Road, Bellefonte, PA).

Apparatus

The ML consists of one vehicle (Ford F-555), a satellite communication system and two gas chromatograph/mass spectrometers (GC/MS) specifically designed for detecting toxic industrial chemicals in air, soil and water. The advanced analytical instruments are complemented by a series of field instruments for the quick detection of volatile compounds, metals and other chemicals. The GC/MS conditions used in this study were:

1. GC/MSD: Agilent 6850/5973 GC/MSD with ChemStation computer system.
2. Column: HP-5MS (5% phenyl methyl siloxane).
3. Temperature program: rate 20°C/min, initial temperature 80°C, final temperature 300°C and run time 14.5 min.
4. MSD/SIM setup: auto tune, DFTPP tune, toxaphene target ion 159 m/z, reference ions 231 m/z and 233 m/z..
5. Internal standard: 2-florobiphenyl target ion 172 m/z, reference ions 170 m/z and 171 m/z.
6. Surrogate: decachlorobiphenyl target ion 241 m/z, reference ions 170 m/z and 172 m/z.

Sample and Standard Preparation

Extraction: Approximately 5g soil were weighed into a 40 mL VOA vial, and 5mL of a hexane solution containing 2-fluorobiphenyl (1ug/mL) and decachlorobiphenyl (1ug/mL) as internal standard and surrogate, respectively, were added. The vial was extracted for approximately 3 min on a vortex mixer and approximately 1 mL of the top layer was taken into an autosampler vial for GC/MSD injection. If the soil samples were wet, anhydrous Na₂SO₄ (ca. 1.0g) was premixed before extraction.

Standards: Six level standards (0.5, 1.0, 2.0, 4.0, 8.0 and 10 ug/mL) were made from soil matrix blanks.

Quantitation retention time: the average of four retention time peaks (9.57, 9.91, 10.65 and 11.15 min) was used.

RESULTS AND DISCUSSION

Gas chromatogram peak retention time and peak area, as well as mass spectrum and ion abundance have been successfully used for volatile and semi-volatile organic compound identification and quantitation. But multi-component analytes, such as toxaphene, aroclors and chlordane present unusual difficulties due to their undefined peaks, multi-humps, and weathering effect changes. As such, these compounds present an interesting challenge. Furthermore, Method 8270C (2) has suggested that the recommended method to test these analytes is Method 8081A (3), i.e., using Gas Chromatography/electron capture detector (GC/ECD), rather than GC/MSD because of sensitivity limitations. A US Office of Inspector General Ombudsman Report recommended using chemical ionization technique to monitor toxaphene degradation products by negative ion mass spectrometry (NIMS) (4). However the ML's on-board GC/MSDs are standard-issue instruments for homeland security rapid identification; and a GC/MSD with Automatic Mass Spectrum Deconvolution Identification Software (AMDIS) superbly detects chemical agents at trace levels. Furthermore, space

limitations make it infeasible to accommodate additional instruments such as a GC/ECD and GC/NIMS with their on-board computer systems. With these considerations in mind, a simplified method to analyze toxaphene by GC/SIM for site characterization was developed to respond to the site mitigation project.

Literature review (5) demonstrated successful results by averaging 4 predetermined retention time area counts for quantitation, therefore, 9.57, 9.91, 10.65 and 11.15 min were chosen after toxaphene hump shape pattern evaluation in the total ion chromatogram (TIC). To establish the quantitation table, 6 levels (0.5, 1.0, 2.0, 4.0, 8.0 and 10 ug/mL) standards were used for each retention time. All standards were made from a hexane extraction in pre-tested soil blanks to suppress soil matrix interference, increase the S/N ratio and enhance sensitivity. The correlation coefficient of the 6 level standards for 4 retention times were $r^2 = 0.999$ at 9.57 min, 0.997 at 9.91 min, 0.999 at 10.65 min and 0.999 at 11.15 min. Internal standard, 2-fluorobiphenyl, was used to obtain relative response factors in quantitation and surrogate decachlorobiphenyl was added into each sample for method recovery data.

The ML staff received 36 samples from the on-site project manager which were prepared according to the SOP (6). The samples were placed on the autosampler injector for an overnight run and the data were reviewed and processed the following day. The non-detected (ND) samples were screened out by visual comparison or by overlaying the extracted ion (159 m/z) chromatogram to the chromatogram of standards, the extracted ion chromatogram of which is presented in Figure 2. Because of the unique shape of toxaphene, this is a very effective way to differentiate negative samples from positive samples. One ND sample and the 8.0 ppm toxaphene positive sample are presented in Figures 3 and 4, respectively. The results of the positive samples were calculated based on the average of 4 retention time reported values, and the results are presented in Table 1 and Table 2. The average surrogate (decachlorobiphenyl) recovery %, SD and CV % were 92.3, 12.2 and 13.2 from 36 samples respectively.

Development plans for a simple extraction and cleanup procedure are being considered for the near future, and a comparison against standard methods will be undertaken.

CONCLUSIONS

Site Mitigation is a major part of DTSC's responsibility. The ML scientists used their simplified GC/MS/SIM method to complete 36 samples in less than 3 days and to detect 6 contaminated hot spots on the site. This simplified method was developed for quick on-site screening and site characterization purposes. This method is simple, fast and easy to use as no lengthy extraction and cleanup procedures are necessary. However, this method may be biased towards false positives rather than false negatives; consequently, development plans for simple extraction and cleanup procedures are being considered for the near future.

REFERENCES

- (1) DTSC, SOP 1000-S, Mobile Laboratory Activation and Deployment (2007)
- (2) EPA Method 8270C, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). Test methods for Evaluating Solid Waste, Physical/Chemical methods (SW-846).
- (3) EPA method 8081A, Organochlorine Pesticides by Gas Chromatography, Test Methods for Evaluating Solid Waste, Physical/Chemical methods (SW-846).
- (4) US Office of Inspector General Ombudsman Report (No. 2006-P- 00007). More Information Is Needed On Toxaphene Degradation Products, December 16, 2005.
- (5) PerkinElmer Instruments, Environmental Application Note.
- (6) DTSC, SOP 1018-S, Screening Method for Toxaphene in Soil (2007)
- (7) Food, Testing & Analysis 6, 13-18, 46. 2000

ACKNOWLEDGMENTS

The authors thank Maria Gillette, Project Manager and her associates, Brad Parsons, Jerry Lile and Sam Martinez, for preparing on-site homogenous soil samples. The authors also wish to thank Dr. Bruce La Belle (Division Chief) and Dr. Myrto Petreas (Branch Chief) for their support and encouragement of this research project.

Table 1. Quantitative Results by Averaging Calibrated Results from 4 retention times

Quantitation Report (QT Reviewed)							
Data Path : C:\msdchem\1\DATA\LOSBAN\							
Data File : STD070123A.D							
Acq On : 23 Jan 2007 12:25							
Operator : OG /KC							
Sample : STD070123A							
Misc : CHECK CALIB STD 4PPM							
ALS Vial : 12 Sample Multiplier: 1							
Quant Time: Jan 23 13:44:43 2007							
Quant Method : C:\msdchem\1\METHODS\TXPN3LB.M							
Quant Title : TOXAPHENE 3 IONS SIM GCMS							
QLast Update : Tue Jan 23 10:53:28 2007							
Response via : Initial Calibration							
Internal Standards		R.T.	QIon	Response	Conc	Units	Dev(Min)
1) Internal Std(2-FBP)	R...	5.065	172	1277116	1.00	ppm	0.00
System Monitoring Compounds							
6) Surrogate RT	12.72	12.717	214	72864	1.11	ppm	0.01
Spiked Amount	1.000			Recovery	=	111.00%	
Target Compounds							
2) Toxaphene RT9.57		9.572	159	1554m	4.61	ppm	Qvalue
3) Toxaphene RT9.91		9.910	159	2116	4.07	ppm	90
4) Toxaphene RT10.65		10.652	159	4481	4.18	ppm	83
5) Toxaphene RT11.15		11.157	159	3363m	4.65	ppm	

(#)= qualifier out of range (m)= manual integration (+)= signals summed							
TXPN3LB.M Tue Jul 24 10:05:22 2007				Average = 4.38 ppm			

Table 2. Results of Toxaphene and Surrogate Recovery in soil samples

ECL Number	Collector's Number	Toxaphene, mg/Kg	Decachlorobiphenyl, %
AQ01031	CVF P-1	< 1.8	81.0
AQ01032	CVF P-2	8.0	81.0
AQ01033	CVF P-3	6.8	82.0
AQ01034	BH-10-6-9	< 1.8	76.0
AQ01035	CVF-13-6-9	< 1.8	79.0
AQ01036	POND 1-24	< 1.8	85.0
AQ01037	POND 2-12	< 1.8	87.0
AQ01038	POND 2-2	< 1.8	86.0
AQ01039	POND 2-S	< 1.8	88.0
AQ01040	POND 3-24	< 1.8	88.0
AQ01041	POND 4-5	< 1.8	88.0
AQ01042	POND 4-12	< 1.8	80.0
AQ01043	POND 4-2	< 1.8	77.0
AQ01044	POND 5-S	< 1.8	87.0
AQ01045	CVF POND 6-1	< 1.8	78.0
AQ01046	CVF POND6-2	< 1.8	78.0
AQ01047	CVF POND 6-S	< 1.8	81.0
AQ01048	CVF POND 7-1	< 1.8	77.0
AQ01049	CVF POND7-2	< 1.8	99.0
AQ01050	CVF POND 7-S	< 1.8	94.0
AQ01051	POND 5-1	< 1.8	89.0
AQ01052	POND 5-2	< 1.8	86.0
AQ01053	CVF 12-6-9	< 1.8	87.0
AQ01054	CVF 14-3-6	< 1.8	111.0
AQ01055	CVF 14-12	< 1.8	113.0
AQ01056	CVF 15-3	< 1.8	113.0
AQ01057	CVF 16-3-6	30.0	114.0
AQ01058	CVF 18-S	< 1.8	105.0
AQ01059	CVF P-2-1	< 1.8	107.0
AQ01060	CVF P2-2	< 1.8	104.0
AQ01061	CVF P2-3	< 1.8	103.0
AQ01062	CVF 18-3-6	8.9	103.0
AQ01063	CVF 18-1	5.7	104.0
AQ01064	CVF 19-1	< 1.8	102.0
AQ01065	CVF 19-S	< 1.8	102.0
AQ01066	CVF 19-3-6	4.0	106.0
MEAN			92.3
SD			12.2
CV			13.2
n			36

Figure 1. Site Mitigation Sampling Plan and photograph of abandoned site

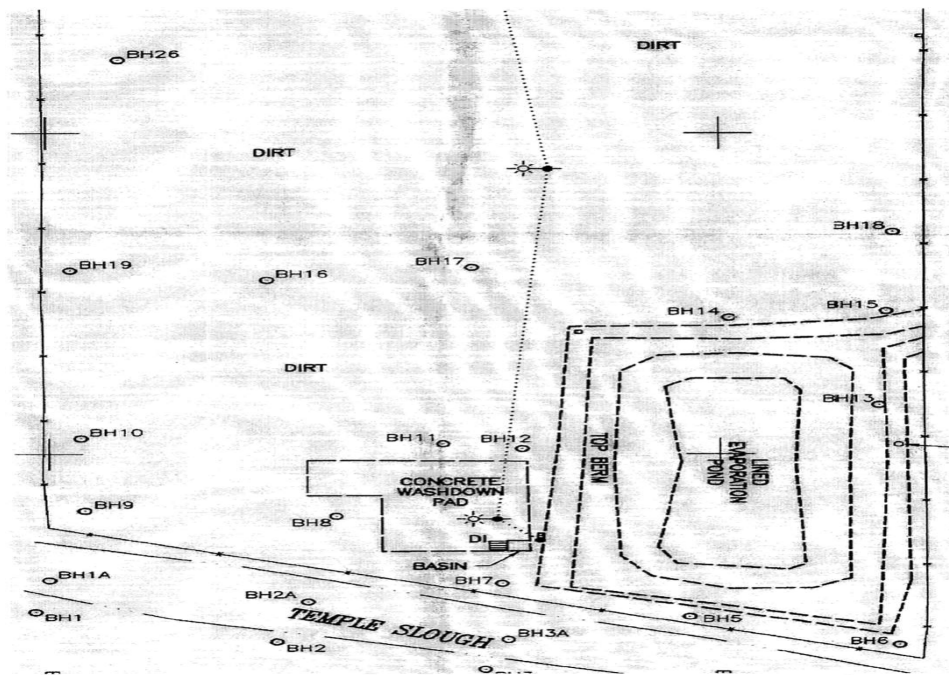


Figure 2. Chromatogram of the extracted ion 159 m/z from toxaphene standard at 4 ppm.

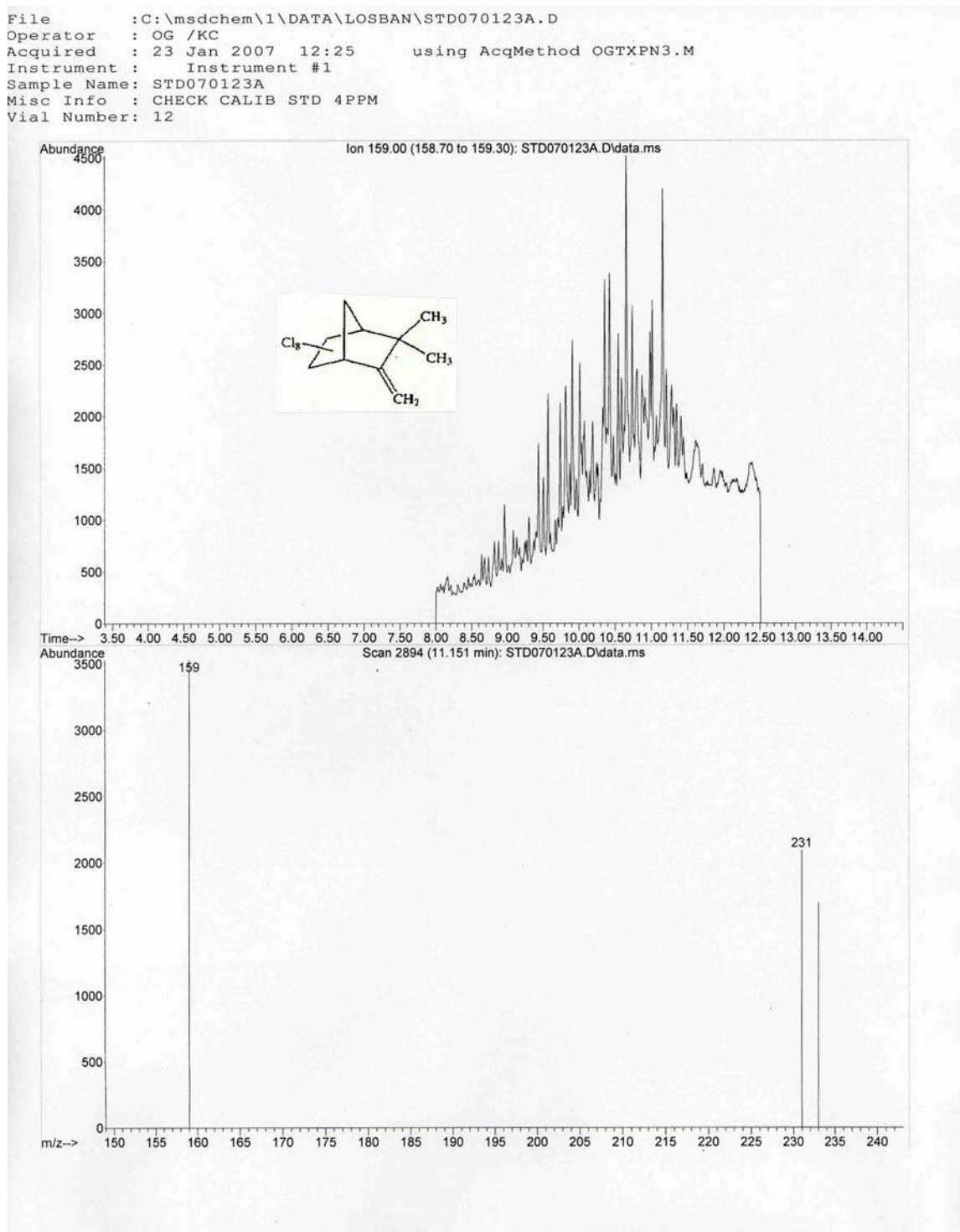


Figure 3. Chromatogram of a non-detected (ND) toxaphene soil sample.

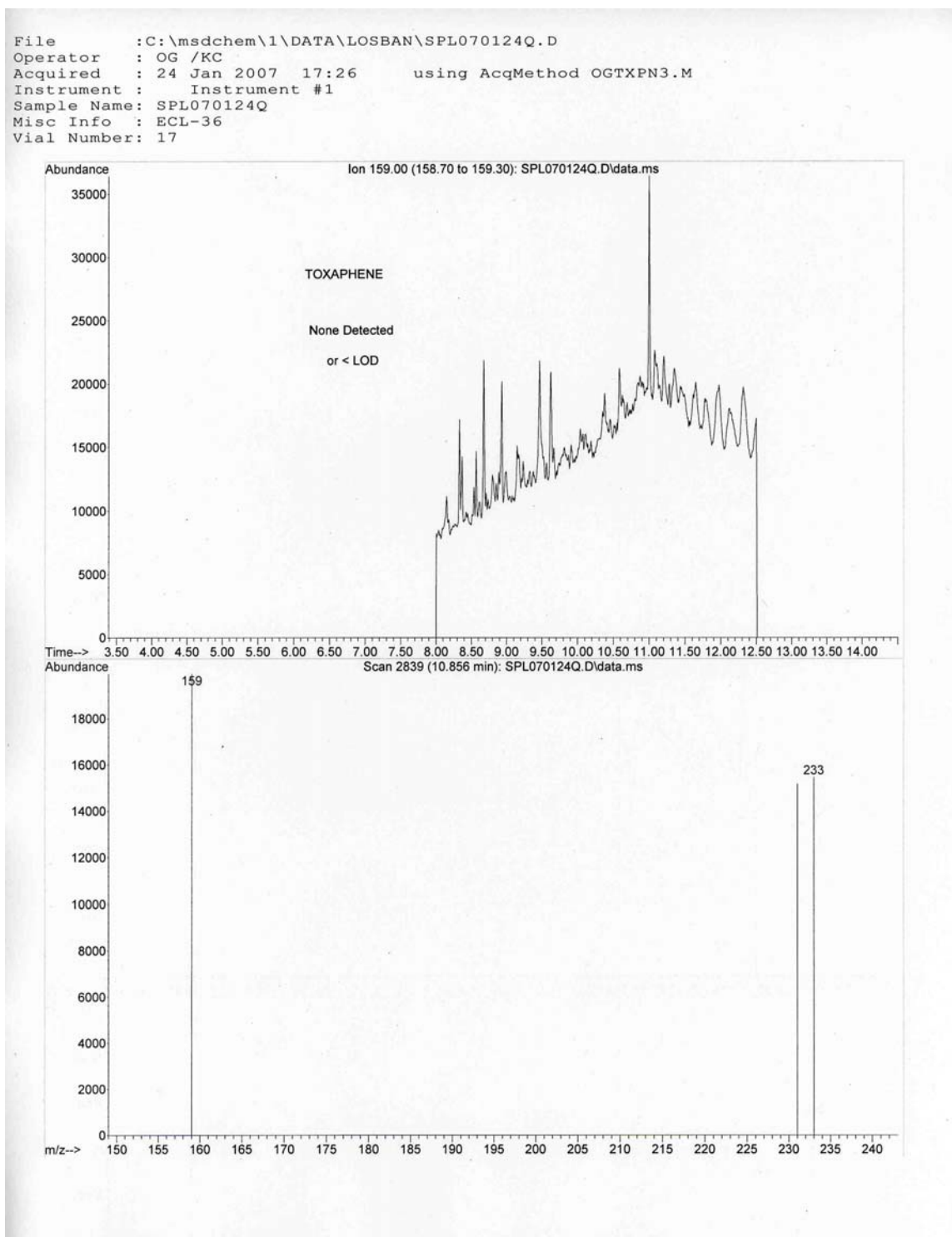
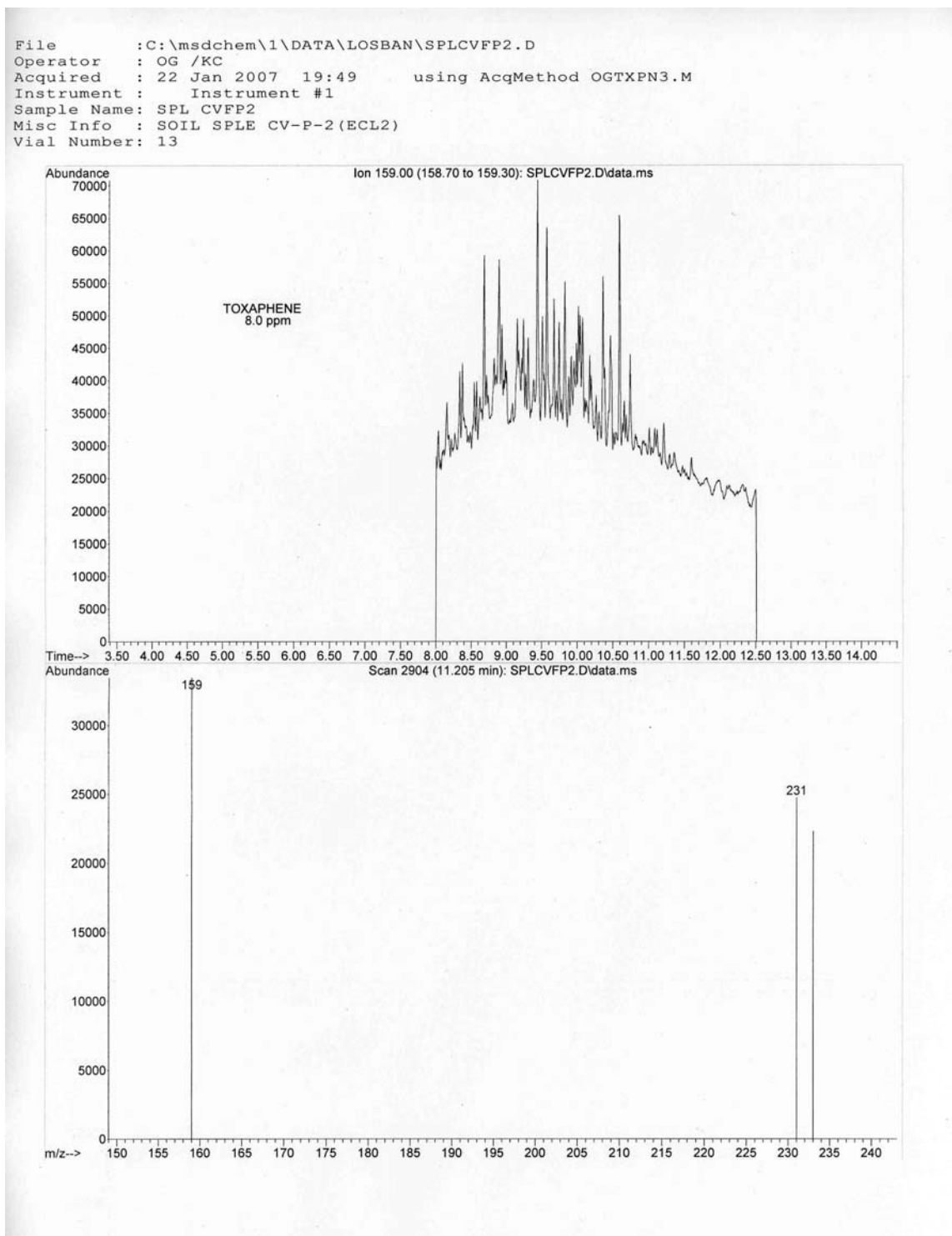


Figure 4. Chromatogram of toxaphene found in a positive soil sample.



Appendix – Sample Reports

For ECL No.s AQ01031
to AQ01066

Auth. No.	06EC0154
Page	1
of	8

Date Collected:	<u>1/22-23/2007</u>
Date Received by Lab:	<u>1/22-23/2007</u>
Date Extracted:	<u>1/22-24/2007</u>
Data Analyzed:	<u>1/22-24/2007</u>
Extraction Method:	Hexane Extrn
Analysis Method:	GC/MSD

Extraction Holding Time Met ? : YES
Analysis Holding Time Met ? : YES

Extraction Methods:	EPA 3510C For aqueous samples; Separatory funnel extraction with methylene chloride. Solvent exchange to hexane.
	EPA 3546 For solid samples; microwave extraction with hexane/acetone, followed by solvent exchange to hexane.
	EPA 3550B For solid samples; sonication extraction with hexane/acetone, followed by solvent exchange to hexane.
	EPA 3580A For oils & organic liquid samples; Solvent dilution with hexane.
Cleanup Method:	EPA 3620 Florisil column cleanup; (Normally not performed unless otherwise mentioned in the report).
Analytical Method:	EPA 8081A Analysis by DB-1701 capillary column GC/EC & confirmation by DB-5 capillary column

[illegible]

Surrogate Standard Recovery:		Unit: Percent (%)					
DECACHLOROBIPHENYL	051-24-3	81.0	81.0	82.0	76.0	79.0	101

Note: QL = Quantitation Limit = Lowest calibration standard x dilution factor
ND = Not detected or detected but below QL

Comments:

Signature: _____

Signature: _____

Signature: _____

3/07/07
Date:

3.7.07

Date: 3707

Date: 2.7.07

For ECL No.s AQ01031
to AQ01066

Signature: _____

Date: 2/10/17

For ECL No.s AQ01031
to AQ01066

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of 8

Date Collected: 1/22-23/2007
Date Received by Lab: 1/22-23/2007
Date Extracted: 1/22-24/2007
Data Analyzed: 1/22-24/2007
Extraction Method: Hexane Extr
Analysis Method: GC/MS

Extraction Holding Time Met ? : YES
Analysis Holding Time Met ? : YES

Extraction Methods:	EPA 3510C For aqueous samples; Separatory funnel extraction with methylene chloride. Solvent exchange to hexane.
	EPA 3546 For solid samples; microwave extraction with hexane/acetone, followed by solvent exchange to hexane.
	EPA 3550B For solid samples; sonication extraction with hexane/acetone, followed by solvent exchange to hexane.
	EPA 3580A For oils & organic liquid samples; Solvent dilution with hexane.
Cleanup Method:	EPA 3620 Florisil column cleanup; (Normally not performed unless otherwise mentioned in the report).
Analytical Method:	EPA 8081A Analysis by DB-1701 capillary column GC/ECD & confirmation by DB-5 capillary column GC/MS.

Surrogate Standard Recovery:		Unit: Percent (%)					
DECAChlorOBIPHENYL	051-24-3	78.0	81.0	77.0	99.0	94.0	101

Comments:

Signature: _____

Signature: _____

Signature: _____

3/07/07
Date:

3.7.c
Date: ()

3.7.07
Date:

For ECL No.s AQ01031
to AQ01066

Page	6
of	8

Date Collected: 1/22-23/2007
Date Received by Lab: 1/22-23/2007
Date Extracted: 1/22-24/2007
Data Analyzed: 1/22-24/2007
Extraction Method: Hekane Extra
Analysis Method: GCMSD

Extraction Holding Time Met?: YES
Analysis Holding Time Met?: YES

Extraction Methods: EPA 3510C For aqueous samples; Separatory funnel extraction with methylene chloride. Solvent exchange to hexane.
EPA 3546 For solid samples; microwave extraction with hexane/acetone, followed by solvent exchange to hexane.
EPA 3550B For solid samples; sonication extraction with hexane/acetone, followed by solvent exchange to hexane.
EPA 3580A For oils & organic liquid samples; Solvent dilution with hexane.
Cleanup Method: EPA 3620 Florisil column cleanup; (Normally not performed unless otherwise mentioned in the report).
Analytical Method: EPA 8081A Analysis by DB-1701 capillary column GC/ECD & confirmation by DB-5 capillary column GC/MS.

Surrogate Standard Recovery:		Unit: Percent (%)					
DECACHLOROBIPHENYL	051-24-3	113	114	105	107	104	101

Comments:
* Detected value exceeded linear calibration. This is an estimate.

Signature: _____

Signature:

Signature: _____

Date: _____

Date: _____

Date: 27.0

For ECL No.s AQ01031
to AQ01066

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of 8

Date Collected:	<u>1/22-23/2007</u>
Date Received by Lab:	<u>1/22-23/2007</u>
Date Extracted:	<u>1/22-24/2007</u>
Data Analyzed:	<u>1/22-24/2007</u>
Extraction Method:	Hexane Extrn
Analysis Method:	GC/MSD

Extraction Holding Time Met ?:	<u>YES</u>
Analysis Holding Time Met ?:	<u>YES</u>

Extraction Methods: EPA 3510C For aqueous samples; Separatory funnel extraction with methylene chloride. Solvent exchange to hexane.
EPA 3546 For solid samples; microwave extraction with hexane/acetone, followed by solvent exchange to hexane.
EPA 3550B For solid samples; sonication extraction with hexane/acetone, followed by solvent exchange to hexane.
EPA 3580A For oils & organic liquid samples; Solvent dilution with hexane.
Cleanup Method: EPA 3620 Florisil column cleanup; (Normally not performed unless otherwise mentioned in the report).
Analytical Method: EPA 8081A Analysis by DB-1701 capillary column GC/ECD & confirmation by DB-5 capillary column.

Surrogate Standard Recovery:				Unit: Percent (%)			
DECACHLOROBIPHENYL	051-24-3	103	103	104	102	102	101

Note: QL = Quantitation Limit = Lowest calibration standard x dilution factor
ND = Not detected or detected below QL

Comments:

Signature: _____

Moelam Grill
Signature: /

Signature: _____

Signature: K.C. King

Signature: _____

Date: 3/07/07

3.7.07

Date: 7-7-89

Date: 2/10/1

For ECL No.s AQ01031
to AQ01083

Date Collected:	<u>1/22-23/2007</u>
Date Received by Lab:	<u>1/22-23/2007</u>
Date Extracted:	<u>1/22-24/2007</u>
Data Analyzed:	<u>1/22-24/2007</u>
Extraction Method:	Hexane Extrn
Analysis Method:	GC/MSD

Extraction Holding Time Met ? : YES
Analysis Holding Time Met ? : YES

Extraction Methods: EPA 3510C For aqueous samples; Separatory funnel extraction with methylene chloride. Solvent exchange to hexane.
EPA 3546 For solid samples; microwave extraction with hexane/acetone, followed by solvent exchange to hexane.
EPA 3550B For solid samples; sonication extraction with hexane/acetone, followed by solvent exchange to hexane.
EPA 3580A For oils & organic liquid samples; Solvent dilution with hexane.
EPA 3620 Florisil column cleanup; (Normally not performed unless otherwise mentioned in the report).

Cleanup Method: EPA 8081A Analysis by DB-1701 capillary column GC/ECD & confirmation by DB-5 capillary column

Surrogate Standard Recovery:			Unit: Percent (%)		
DECACHLOROBIPHENYL	051-24-3	106			101

Comments:

Date:

Date: _____

Date: